



(19) Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number : **0 352 067 B1**

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification :
03.03.93 Bulletin 93/09

(21) Application number : **89307261.1**

(22) Date of filing : **18.07.89**

(51) Int. Cl.⁵ : **C10M 163/00, C10M 141/12,**
// (C10M141/12, 129:06,
129:70, 129:72, 139:00),
(C10M163/00, 129:06,
129:70, 129:72, 159:18),
C10N10:08, C10N40:00

(54) Lubrication boosting additives comprising organic titanium compounds and lubricating oil compositions comprising the same.

(30) Priority : **20.07.88 JP 180999/88**

(43) Date of publication of application :
24.01.90 Bulletin 90/04

(45) Publication of the grant of the patent :
03.03.93 Bulletin 93/09

(84) Designated Contracting States :
DE FR GB IT

(56) References cited :
WO-A-87/04454
GB-A- 866 054

(56) References cited :
US-A- 3 398 170
PATENT ABSTRACTS OF JAPAN, vol. 11, no.
307 (C-450)[2754], 7th October 1987, page 33 C
450

(73) Proprietor : **WAKO TECHNICAL CO., LTD.**
15-7, Kitami 9-chome
Setagaya-ku Tokyo (JP)

(72) Inventor : **Watanabe, Ryoji**
1-22, Gotenyama-cho
Hirakata-shi Osaka (JP)

(74) Representative : **Myerscough, Philip Boyd et al**
J.A.Kemp & Co. 14, South Square Gray's Inn
London, WC1R 5EU (GB)

EP 0 352 067 B1

Note : Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Description

This invention relates to lubrication boosting additives which, when added to lubricating oils for use in power engines, can improve load bearing properties of the oils and can prevent wear of the power engines while mitigating the lowering of an energy efficiency owing to the friction.

As is well known in the art, lubrication boosting additives have been widely used in order to improve lubricating characteristics of lubricating oils. GB-A-866054 discloses the use of an organic titanium compound and a dicarboxylic acid in amounts sufficient to increase the load bearing property of an oil. Typical examples of commercially sold additives include suspensions of polytetrafluoroethylene (PTFE) and molybdenum sulfide in the form of fine powder. Polytetrafluoroethylene is a resin which has good lubricating characteristics and a high chemical resistance, but is inconveniently insoluble in almost all the types of solvents, thus making it impossible to use the PTFE resin as a solution. This is why the PTFE resin is used as a fine powder suspended in a medium. However, the use of the suspension presents a serious problem with respect to its compatibility with or dispersability in lubricating oil. For instance, the fine powder may settle in the suspension prior to use or after mixing with lubricating oil. Alternatively, the fine powder may deposit in power engines or may clog filters used in association with the engines.

Moreover, the fine powder of PTFE or molybdenum disulfide rarely contributes to the improvement of the load bearing properties when added to lubricating oils.

We have already proposed in US-A-4,826,614 an oil boosting additive which comprises a fluororesin and a phthalic ester dissolved in an organic solvent. This is very effective for use as an additive to lubricating oils which are employed in power engines. In this additive, the fluororesin is used in large amounts and is relatively expensive.

The invention provides a lubrication boosting additive which comprises 1 part by weight of an organic titanium compound soluble in an organic solvent, from 6 to 60 parts by weight of an organic solvent for the organic titanium compound, and from 10 to 1000 parts by weight of a phthalic ester.

The organic titanium compound improves the load bearing characteristics when added to lubricating oils while the phthalic ester improves the wear resistance. The additive of the invention can increase power output and can suppress noises of engine systems, such as internal combustion engines, when applied to lubricating oils for use in the engine systems. The additive also can reduce fuel cost and can prolong the life of parts when used in lubricating oils for internal combustion engines of motor vehicles.

When added to lubricating oil, the lubrication boosting additive is used in an amount of from 0.01 to 10 g, calculated as the organic titanium compound, per liter of the lubricating oil.

The organic titanium compound which is one of the ingredients in the lubrication boosting additive of the invention should be soluble in the organic solvent. In general, organic titanium compounds have been developed and used as a water repellent, a surface treating agent and a surface film-forming ingredient for a specific type of lamp. The organic titanium compounds useful in the present invention may be any known organic titanium compound which is soluble in ordinary organic solvents, including those used for the treatment of a specific type of lamp. Specific and preferable examples of the organic titanium compounds include tetraalkoxy titanium compounds such as tetrakisopropoxy titanium and tetra-n-butoxy titanium, titanium acylate compounds such as alkoxy-polytitanium acylate, and titanium chelate compounds such as titanium acetylacetone.

The solvents used to dissolve the organic titanium compound include non-aqueous alcohols and esters. Preferable examples of the solvent include methyl alcohol, ethyl alcohol, isopropyl alcohol, isobutyl alcohol, ethyl acetate, butyl acetate and ethoxyethyl acetate. These solvent may be used singly or in combination. Of these, ethyl alcohol and/or ethyl acetate is preferred.

The phthalic acid esters improve a wear resistance which may be slightly lowered by the addition of the soluble organic titanium compound. Examples of the phthalic esters include dibutyl phthalate, dioctyl phthalate and diisodecyl phthalate. Of these, dibutyl phthalate and dioctyl phthalate are preferred.

The amounts of the respective ingredients may depend upon the types of lubricating oil, organic titanium compound, solvent and phthalic ester. In general, the solvent is used in an amount of from 6 to 60 parts by weight (hereinafter referred to simply as parts), preferably from 10 to 30 parts and the phthalic ester is used in an amount of from 10 to 1000 parts, preferably from 50 to 500 parts, each based on unit part of the organic titanium compound.

The lubrication boosting additive of the invention is used in the form of a solution but may contain a small amount of insoluble matters. When the amount of the phthalic ester increases, compatibility with soluble organic titanium compound and a lubricating oil may reduce to a slight extent. Such an increase in amount will tend to improve the load bearing properties of lubricating oils attributable to the soluble organic titanium compound.

Preferable lubrication boosting additives of the invention should comprise 1 part of a soluble organic tita-

nium compound, from 3 to 30 parts, preferably from 5 to 20 parts, of ethyl alcohol and from 3 to 30 parts, preferably from 5 to 20 parts, of ethyl acetate, and from 10 to 1000 parts, preferably from 50 to 500 parts, of dioctyl phthalate.

The soluble organic titanium compound may be formulated as it is or after dissolution in the solvent.

5 The lubricating oils for use with the lubrication boosting additive of the invention may be any lubricating oil which is ordinarily used in engine systems such as reciprocating engines, turbo-propeller engines and rotary engines and also in movable parts such as bearings. The lubrication boosting additive is added to lubricating oils in amounts of from 0.01 to 10 g, preferably from 0.1 to 4 g, per liter of lubricating oil.

10 In practical applications, it is preferred that the additive of the invention is pre-mixed with a small amount of a lubricating oil. This permits the additive to be more readily mixed with or dispersed in a lubricating oil. For the pre-mixing, a lubricating oil is preferably added to the boosting additive in an amount of from 1 to 300 parts per 10 parts of the soluble organic titanium compound.

15 The present invention is more particularly described by way of example, which should not be construed as limiting the invention.

15 Example

A soluble organic titanium compound used was a solution of an organic titanium compound for lamp coating (available from Ushio Inc.), to which ethyl alcohol, ethyl acetate and dioctyl phthalate were, respectively, added 20 in amounts indicated in the following table, thereby obtaining lubrication boosting additives. These additives were each added to one liter of a lubricating oil (engine oil for automobiles, available from Idemitsu Kosan Co., Ltd.) In amounts, calculated as the organic titanium compound, indicated in the table. The resulting lubricating oil compositions were subjected to measurements of a load bearing property and a wear resistance. These properties were determined by the Soda four ball friction tester and expressed in terms of a load bearing capacity and a diameter of wear defect. The results are shown in the table below.

Table

30 Test No.	Additive Composition (parts by weight)				Amount of Organic titanium in one liter of Lubricating Oil (g)	Lubricating Characteristics	
35	soluble organic alcohol titanium	ethyl acetate	DOP			load bearing capacity (MPa)	wear resist- ance (mm)
40	1	-	-	-	-	0.25	0.59
	2	1	20	10	400	0.40	0.56
45	3	1	10	20	200	0.35	0.56
	4	1	10	20	100	0.35	0.57
50	5	1	20	10	-	0.30	0.62
	6	1	40	40	-	0.30	0.63
	7	1	20	10	-	0.25	0.60

55 As will be apparent from the above results, when DOP is not used (Test Nos. 5 to 7), the load bearing capacity is improved but the wear resistance lowers. However, when DOP is added (Test Nos. 2 to 4), the load bearing capacity is improved with a good wear resistance. When the organic titanium compound is added, the

load bearing capacity of the lubricating oil is significantly improved. This becomes remarkable when the organic titanium compound is used in combination with DOP.

It will be noted that all the additives of the invention were found not to cause phase separation or gelation 3 days after the preparation and could be readily and uniformly mixed with the lubricating oil.

5

Claims

- 10 1. A lubrication boosting additive which comprises 1 part by weight of an organic titanium compound, from 6 to 60 parts by weight of a solvent for said organic titanium compound, and from 10 to 1000 parts by weight of a phthalic ester.
- 15 2. An additive according to claim 1, wherein said organic titanium compound is a tetraalkoxy titanium compound, a titanium acylate compound or a titanium chelate compound.
- 20 3. An additive according to claim 1 or 2, wherein said solvent is ethyl alcohol and/or ethyl acetate.
4. An additive according to claim 1, 2 or 3, wherein the amount of solvent is 10 to 30 parts by weight.
- 25 5. An additive according to any one of the preceding claims wherein said phthalic ester is diethyl phthalate or dibutyl phthalate.
6. An additive according to any one of the preceding claims wherein the amount of phthalic ester is 50 to 500 parts by weight.
- 30 7. An additive according to claim 1 or 2 which comprises a mixed solvent of from 3 to 30 parts by weight of ethyl alcohol and from 3 to 30 parts by weight of ethyl acetate and from 10 to 100 parts by weight of diethyl phthalate.
8. A lubricating oil composition which comprises a lubricating oil and a lubrication boosting additive as claimed in any one of the preceding claims in an amount of from 0.01 to 10 g, calculated as the organic titanium compound, per liter of the lubricating oil.

Patentansprüche

- 35 1. Additiv zur Verbesserung der Schmierung, das 1 Gewichtsteil einer organischen Titanverbindung, 6 bis 60 Gewichtsteile eines Lösungsmittels für diese organische Titanverbindung und 10 bis 1000 Gewichtsteile eines Phthalsäureesters enthält.
- 40 2. Additiv nach Anspruch 1, in dem die organische Titanverbindung eine Tetraalkoxytitanverbindung, eine Titanacylatverbindung oder eine Titanelatverbindung ist.
3. Additiv nach Anspruch 1 oder 2, in dem das Lösungsmittel Ethylalkohol und/oder Ethylacetat ist.
- 45 4. Additiv nach Anspruch 1, 2 oder 3, in dem die Menge des Lösungsmittels 10 bis 30 Gewichtsteile beträgt.
5. Additiv nach einem der vorausgehenden Ansprüche, in dem der Phthalsäureester Diethylphthalat oder Dibutylphthalat ist.
6. Additiv nach einem der vorausgehenden Ansprüche, in dem die Menge des Phthalsäureesters 50 bis 500 Gewichtsteile beträgt.
- 50 7. Additiv nach Anspruch 1 oder 2, das ein gemischtes Lösungsmittel aus 3 bis 30 Gewichtsteilen Ethylalkohol und 3 bis 30 Gewichtsteilen Ethylacetat sowie 10 bis 100 Gewichtsteile Diethylphthalat enthält.
- 55 8. Schmierölmischung, die ein Schmieröl und ein Additiv zur Verbesserung der Schmierung nach einem der vorausgehenden Ansprüche in einer Menge von 0,01 bis 10 g, berechnet als organische Titanverbindung, pro Liter Schmieröl enthält.

Revendications

1. Additif renforçant la lubrification, qui comprend une partie en poids d'un dérivé organique du titane, de 6 à 60 parties en poids d'un solvant pour ledit dérivé organique du titane, et de 10 à 1000 parties en poids d'un ester phthalique.
5
2. Additif selon la revendication 1, dans lequel ledit dérivé organique du titane est un tétra(alcoxy)titane, un dérivé acylé du titane ou un chélate de titane.
- 10 3. Additif selon la revendication 1 ou 2, dans lequel ledit solvant est l'alcool éthylique et/ou l'acétate d'éthyle.
4. Additif selon la revendication 1, 2 ou 3, dans lequel la quantité de solvant est de 10 à 30 parties en poids.
- 15 5. Additif selon l'une quelconque des revendications précédentes, dans lequel ledit ester phthalique est le phtalate de diocyle ou le phtalate de dibutyle.
6. Additif selon l'une quelconque des revendications précédentes, dans lequel la quantité d'ester phthalique est de 50 à 500 parties en poids.
- 20 7. Additif selon la revendication 1 ou 2, qui comprend un solvant mixte, constitué de 3 à 30 parties en poids d'alcool éthylique et de 3 à 30 parties en poids d'acétate d'éthyle, et de 10 à 100 parties en poids de phtalate de diocyle.
- 25 8. Composition d'huile lubrifiante, qui comprend une huile lubrifiante et un additif renforçant la lubrification, tel que revendiqué dans l'une quelconque des revendications précédentes, en une quantité de 0,01 à 10 g, calculée en dérivé organique du titane, par litre d'huile lubrifiante.

30

35

40

45

50

55